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Solvent-free Synthesis of Cyclic Carbonates from CO_2 and Epoxides Catalyzed by Reusable Alumina-supported Zinc Dichloride

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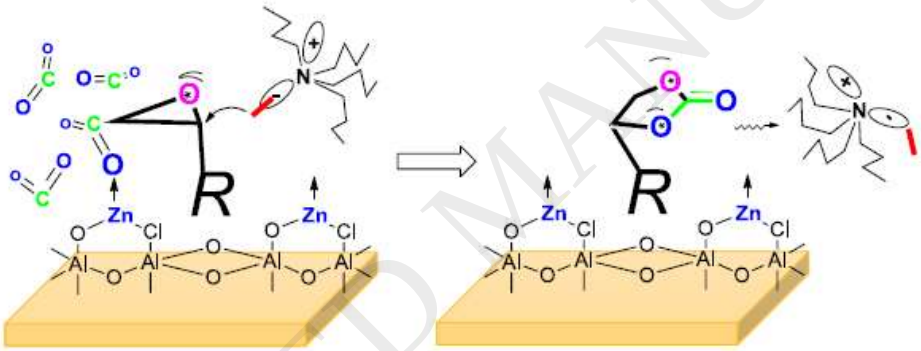
Graphical abstract



HIGHLIGHTS

- The first heterogeneous $ZnCl_2$-catalyzed carboxylation of epoxides is presented.
- $ZnCl_2/Al_2O_3$-TBAI is efficient, cheap, easily prepared and applied catalytic system.
- The reaction typically occurs under mild (60ºC, 4 atm) and solvent-free conditions.
- The catalyst ($ZnCl_2/Al_2O_3$) and nucleophilic additive (TBAI) have been reused in five cycles.
- The catalyst also works in the reaction of epoxides with CS_2 to form thiocarbonates.

Abstract: There is an ongoing interest to advance in the production of cyclic carbonates from carbon dioxide and epoxides under sustainable conditions. The $ZnCl_2/Al_2O_3$-TBAI system has evinced to be a cheap, simple, readily accessible and reusable catalyst for the reaction of carbon

dioxide with aromatic, aliphatic, cyclic and fluorinated epoxides with a low metal loading under solvent-free and mild conditions. This system has been also shown to be adequate for the reaction of epoxides with carbon disulfide to form the sulfur-containing cyclic carbonate analogs.

Keywords: carbon dioxide, epoxide, zinc dichloride/alumina, cyclic carbonate, heterogeneous catalysis

1. Introduction

Carbon dioxide is, among others (CO, CO_2, CH_4), the most appealing C1 carbon source because of being renewable, nontoxic, non-flammable, readily available and relatively inexpensive. It can be converted into fuels, materials and value-added chemicals by replacing other environmentally less benign substances with a lower E-factor impact [1]. It is a crucial building block for the synthesis of useful organic compounds [2–5], being its reaction with epoxides [6, 7] of paramount importance for the industrial preparation of carbonates (e.g., dimethyl carbonate, diphenyl carbonate, ethylene carbonate, propylene carbonate and glycerol carbonate) [8, 9] and polycarbonates [10]. Cyclic carbonates, apart from being present in natural products and potential pharmaceuticals, have found manifold applications in different disciplines; for instance, as electrolytes in lithium-ion batteries, as polar aprotic solvents and as synthetic intermediates [11-14].

Besides being a 100% atom-economical process, the high thermodynamic stability of the CO_2 molecule [15] makes the intervention of catalysts imperative for activating the implicated reagents [16]. Homogeneous catalysis and, to some extent, organocatalysis, dominate over heterogeneous catalysis, typically, in the presence of an ammonium salt [6, 17–19]. A great advance in the field was made by North et al., who introduced the binuclear Al-salen [20, 21] and salphen [22, 23] complexes, together with a polystyrene-immobilized counterpart [24], as highly efficient catalysts for the carboxylation of terminal epoxides at room temperature and atmospheric pressure. Notwithstanding this research merit, the catalysts preparation requires multistep synthesis and the immobilized catalyst suffers from deactivation. Mononuclear Al-salen complexes [25] were shown to be also effective in the carboxylation of terminal epoxides, though higher temperature and longer reaction time were mandatory.

Lately, new catalytic systems have emerged with the aim to upgrade the performance of the epoxide-CO_2 cycloaddition, namely: CaI_2-(PEG DME 500) [26], CaI_2-crown ether [27, 28], tri-Co complex containing amine-bis(benzotriazole phenolate) ligands (in combination with TBAC) [29], highly active Al-aminotriphenolate [30] and Al-porphyrin based catalysts [31], Mn(II)-pyridin-4-yl-phosphonate MOF-TBAB [32], Ln(III)-coordinated polymers-TBAB [33] and La-heteroscorpionate-TBAB [34]. Notably, the formation of the cyclic carbonates could be accomplished not only in the

presence of rather sophisticated complexes but also with simple catalysts such as $MgCl_2$ (DMF, 100 ºC) [35].

The combination of a ZnX_2 Lewis acid catalyst with an ammonium salt has been also successfully exploited in the epoxide carboxylation [36]. For instance, TBAI with Zn-salphen [37, 38], bis-(Zn-salphen) [39], Zn-azatrane [40], Zn-pyrrolidine [41] complex or Zn-MOF [42, 43] allowed to carry out the reaction under mild conditions in good yields. The ammonium salt could be replaced with an ionic liquid [44] to furnish good yields with the assistance of a ligand-free zinc salt at 30 ºC and 1 atm CO_2 [45]. Ema et al. inserted an ammonium-fragment linker into zinc porphyrinate [46–48], with the resulting catalyst showing high TONs and TOFs, albeit under harsh reaction conditions (120 ºC, 17 atm). A system based on the Zn cluster $Zn_4(TFA)_6O$-TBAI, insensitive to moisture and gaseous impurities, was effective under mild conditions (25°C, 1 atm) but relatively longer reaction time was needed (up to 20 h) [49]. As an alternative to the activation of the epoxide, CO_2 can be activated by N-heterocyclic carbenes (NHC) through the formation of NHC-CO_2 adducts [50]; in this sense, the NHC-$ZnBr_2$ system catalyzed the cycloaddition of CO_2 to epoxides at atmospheric pressure (80 ºC, DMSO) [51].

Metal-free organocatalytic systems look very attractive and green [18]. As recent examples, highly active cavitand-based polyphenol catalyst allowed to get good-to-excellent yields of both mono- and disubstituted carbonates in 18 h at 50 ºC and 10 bar of CO_2 in the presence of TBAI [52]; using squaramide derivatives, terminal carbonates were obtained in shorter time at higher temperature [53], whereas harsher conditions were necessary for internal epoxides. Alkyl ammonium and phosphonium salts themselves are active organocatalysts but they are difficult to recover and are deployed in quasi-equimolar amounts with respect to the substrate.

In spite of the fact of the good catalytic behavior manifested by the aforementioned catalysts, their homogeneous nature precludes reutilization and limits their practical application, especially of those involving tedious preparation procedures. In this vein, heterogeneous catalysis offers the possibility of catalyst recovery and reuse, hence making the whole process more sustainable [54]. Even though heterogeneous catalysts are characterized by a longer life than the homogeneous counterparts, the former have been much less investigated than the latter in the epoxide carboxylation, in part, because they are considered less active and require more severe conditions to reach a satisfactory yield. For instance, the silica/TBAB-catalyzed CO_2-epoxide cycloaddition needed high catalyst loading, pressure (40 atm) and temperature (90 ºC) [55]. Likewise, elevated temperature (100–140 ºC) and pressure (10–45 atm) or prolonged reaction time (up to 48 h) had to be applied for ionic liquids [56] grafted onto different supports [57–61]. A Cu^{II} metal-organic hydrogel [62] and indium-based metal organic framework [63] worked under milder conditions but with modest-to-good conversions of the terminal epoxides (32–80%). Recently investigated, the heterogeneous catalysts based on three-

dimensional copper-phosphate grid [64], APTES-modified zirconium oxide on MCM-41 [65], and cobalt-coordinated conjugated microporous polymer (Co-CMP-2) [66] allowed to attain high TONs and TOFs, but excellent yields were achieved only under relatively high pressure and temperature (80–100 ºC, 10–30 atm). Several zinc-containing heterogeneous systems, such as a zinc complex with mesoporous *o*-hydroxybenzene polymers [67], a zeolitic imidazolate framework (ZIF-95) containing Zn atoms [68], a binuclear supramolecular zinc complex with hexadentate ligands [69] or Zn-Mg-Al composite oxides [70] have been reported; although all the catalysts were reused, at least, five times without significant loss of their activity, the reaction conditions were rather harsh (80–140 ºC, 12–50 atm).

Concluding this introduction, we can say that there is a general upsurge of interest in developing sustainable catalysts [71, 72] and reaction media [73] to promote the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions [74]. In an ideal scenario, the catalytic systems should be simple, reusable for several cycles, without toxic reagents, and producing the cyclic carbonates in high yield and selectivity with a minimum generation of waste. In this context, we present herein our endeavor to adhere to these premises and introduce the heterogeneous catalytic system composed of $ZnCl_2$ supported on alumina which, together with a catalytic amount of TBAI, catalyzes the epoxide carboxylation and thiocarboxylation in an efficient manner.

2. Experimental

2.1. General

All starting materials were purchased from Sigma Aldrich and P&M-Invest (http://en.fluorine1.ru/) and were used without any further purification; solvents were dried and deoxygenated using standard procedures. Carbon dioxide gas of 99.99% purity was used. The carboxylation reactions were performed in a 15 mL-capacity glass low-pressure reactor RLP25ML (http://www.openscience.ru) equipped with a gas feeding system, magnetic stirrer and manometer. The NMR spectra of all products were recorded on Bruker Avance 400 and Agilent 400MR spectrometers (^{1}H NMR 400 MHz, ^{13}C NMR 100.6 MHz and ^{19}F NMR 376 MHz) at ambient temperature in $CDCl_3$. The chemical shifts are reported in ppm relative to $SiMe_4$ in the ^{1}H NMR spectra and to chemical shifts of the solvent peaks, as a secondary standard, in the ^{13}C NMR spectra. The chemical shifts are reported in ppm relative to $CFCl_3$ as an internal standard in the ^{19}F NMR spectra. The coupling constants (*J*) are given in Hertz. The GLC-mass spectra were obtained on a LECO Pegasus 4D TOF spectrometer with Agilent GC with RTX-5-MS column. Column chromatography was carried out on Merck silica gel 60 (40–63 μm) with petroleum ether (b.p. 60–90°C) as the eluent.

XRD patterns were recorded on an X-ray diffractometer DRON-3 in the reflection mode with CoKα radiation using θ/2θ scanning technique. FT-IR spectra were obtained in the 750–4000 cm^{-1} spectral

range using a Thermo Nicolet 200 FT-IR instrument. Samples of organic products for IR spectroscopy were used as a thin film. FT-IR/ATR spectra of inorganic specimens were recorded in the 400–8000 cm^{-1} spectral range on FT-IR Tenzor II spectrometer (Bruker) equipped with single reflection diamond ATR module Platinum (Bruker). Mass spectra were recorded using a Varian 431-GC/220-MS spectrometer with EI (electron ionization). The nitrogen adsorption–desorption isotherms were collected at 77 K using an adsorption analyzer Micromeritics ASAP2020 Plus. The pore size distribution was calculated by the BJH (Barrett-Joyner-Halenda) method using the desorption isotherm. The total pore volume (V, mL/g) and the specific surface area (*S*, m^2/g) was determined by the BET (Brunauer-Emmett-Teller) method. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) studies were carried out on a LeoSupra 50VP microscope equipped with an Oxford Instrument XMax detector using a 15 kV accelerating voltage and working distance of 7 nm in a low vacuum mode (N_2, 40 Pa). A VPSE detector was applied with magnifications from 200 to 2500. EDX spectra were recorded using X-Ray microanalysis and, then, assigned to the image of the sample surface. The energy resolution of the EDX detector reached 129 eV for line MnKα (5898.8 eV). The statistical analysis of the obtained micrographs for the determination of the complex composition was performed using ImageJ software.

2.2. Preparation of the Lewis acid/support catalysts

The Lewis acid/support 10 wt% was prepared by grinding the anhydrous Lewis acid (50 mg) with the dry support (450 mg) in agate pounder for 20 minutes at ambient temperature. The resulting homogeneous powder was heated in vacuum for 2 h at 80 ºC.

2.3. General procedure for the reaction of epoxides with CO_2.

The epoxide (4.0 mmol), catalyst (0.024 mmol) and quaternary ammonium salt (0.064 mmol) were added to a 25 mL glass low-pressure reactor (RLP25ML, www.openscience.ru) equipped with a gas feeding system, magnetic stirrer and manometer. The reactor was purged thrice followed by the introduction of CO_2 gas (4 atm, unless otherwise specified). The reaction mixture was stirred at 60 ºC for 6 h (or under other conditions as indicated below for certain compounds). The resulting mixture was cooled to room temperature, centrifuged (no solvent added) and purified by column chromatography (silica gel, petroleum ether). The isolated product was dried under vacuum.

2.3.1. General procedure for the reaction of epoxides with CO_2 in the presence of solvent.

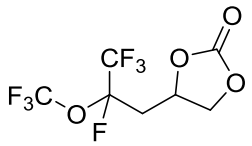
The same general procedure 2.3 was applied but with the addition of solvent (2 mL). After the reaction completion, the resulting mixture was cooled to room temperature, centrifuged, concentrated under vacuum and purified by column chromatography (silica gel, petroleum ether). The isolated product was dried under vacuum.

2.4. Catalyst reutilization procedure.

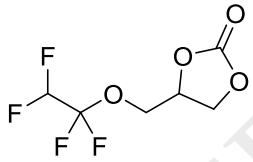
The reaction was carried out as described above in the general procedure 2.3 with propylene oxide for 2 h. The resulting mixture was centrifuged (no solvent added) and the precipitate was dried under vacuum and added to the reactor together with a new loading of reagents. TBAI was recovered from the supernatant by precipitation with diethyl ether (2 mL), followed by centrifugation and drying under vacuum; then, it was used in the next run.

*2.5. Characterization of compounds **2a-o**:*

The NMR spectral data for compounds **2a-k** correspond to those in the literature. (See ESI for more details.)

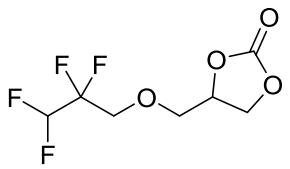


4-(2,3,3,3-Tetrafluoro-2-(trifluoromethoxy)propyl)-1,3-dioxolan-2-one (2l). (24 h, 80 ºC, TBAB as nucleophilic additive). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.07–4.99 (m, 1H), 4.64 (t, *J* = 8.4 Hz, 1H), 4.20–4.15 (m, 1H), 2.82–2.71 (m, 1H), 2.59–2.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 119.5 (qd, J=264.6 Hz, 5.7 Hz), 118.9 (qdq, *J*=286.6 Hz, 32.9 Hz, 5.1 Hz), 107.5 (dq, *J*=261.4, 38.2 Hz), 70.2, 69.1, 36.9 (dd, *J*=21.9 Hz, 7.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –53.4 - –53.6 (m, 3F), –83.2 (dd, *J* = 39.5 Hz, 4.2 Hz, 3F), –130.4 (ddq, *J* = 152.6 Hz, 34.5 Hz, 13.2 Hz, 1F). Anal. calcd for $C_7H_5F_7O_4$: C, 29.39; H, 1.76; F, 46.48; O, 22.37. Found: C, 29.43; H, 1.79; F, 46.46; O, 22.32. IR ($\tilde{\upsilon}$, cm^{-1}): 773, 850, 881, 889, 937, 1012, 1074, 1103, 1128, 1201, 1265, 1311, 1350, 1392, 1485, 1811, 2931, 2991, 3608. EI-MS (*m/z*): 284 (M^+–2, 0.1%), 242 (0.5), 125 (7), 87 (27), 77 (5), 69 (100), 64 (4), 59 (27), 57 (10), 55 (10), 47 (7), 44 (34), 43 (45), 42 (20), 41 (7), 39 (7), 31 (9), 30 (14), 29 (43). (See ESI for spectra).



4-[(1,1,2,2-Tetrafluoroethoxy)methyl]-1,3-dioxolan-2-one (2m). (24 h, 80 ºC, TBAB as nucleophilic additive). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.75 (tt, *J* = 52.8 Hz, 2.7 Hz, 1H), 4.96–4.91 (m, 1H), 4.55 (t, *J* = 8.8 Hz, 1H), 4.34 (dd, *J* = 9.0 Hz, 5.9 Hz, 1H), 4.26 (dd, *J* = 11.7 Hz, 3.1 Hz, 1H), 4.10 (dd, *J* = 11.7 Hz, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 117.0 (td, *J* = 270.6 Hz, 28.7 Hz), 107.3 (tt, *J* =251.2 Hz, 41.3 Hz), 73.2, 65.5, 63.0 (t, *J* =5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –91.6 (dtd, *J* = 145.3 Hz, 5.1 Hz, 2.9 Hz, 1F), –92.3 (dtd, *J* = 145.3 Hz, 5.9 Hz, 3.3 Hz, 1F), –137.0 (dt, *J* = 52.8 Hz, 5.5 Hz, 2F). Anal. calcd for $C_6H_6F_4O_4$: C, 33.04; H, 2.77; F, 34.84; O, 29.34. Found: C, 33.08; H, 2.75; F, 34.81; O, 29.36. IR ($\tilde{\upsilon}$, cm^{-1}): 771, 847, 912, 953, 991, 1049, 1082, 1171, 1209, 1279, 1309, 1402, 1485, 1792, 2357, 2931, 2966, 2999, 3573. EI-MS (*m/z*):

216 (M^+–2, 0.2%), 174 (0.5), 158 (1), 144 (2), 131 (11), 101 (69), 93 (11), 87 (95), 86 (8), 82 (7), 67 (4), 57 (11), 51 (74), 44 (49), 43 (100), 42 (13), 31 (24), 30 (13), 29 (82). (See ESI for spectra).



4-[(2,2,3,3-Tetrafluoropropoxy)methyl]-1,3-dioxolan-2-one (2n). (24 h, 80 ºC, TBAB as nucleophilic additive). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.86 (tt, *J* = 53.0 Hz, 4.7 Hz, 1H), 4.85–4.80 (m, 1H), 4.50 (t, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 8.6 Hz, 5.9 Hz, 1H), 3.99–3.72 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.7, 114.7 (tt, *J* =249.7 Hz, 27.0 Hz), 109.1 (tt, *J* =249.6 Hz, 35.4 Hz), 74.6, 71.3, 68.4 (t, *J* =28.4 Hz), 65.8. ^{19}F NMR (376 MHz, $CDCl_3$, δ): –124.7 (tdt, *J* = 12.7 Hz, 4.5 Hz, 3.8 Hz, 2F), –138.9 (dtd, *J* = 21.9 Hz, 3.8 Hz, 1.9 Hz, 1F), –139.0 (dtd, *J* = 22.8 Hz, 3.7 Hz, 1.5 Hz, 1F). The ^{1}H NMR spectral data correspond to those in the literature [27], ^{13}C and ^{19}F NMR spectra were not previously presented.

2.6. General procedure for the reaction of epoxides with CS_2.

Following the general procedure for the epoxide carboxylation (2.3), a mixture of the epoxide (4 mmol), $ZnCl_2/Al_2O_3$ (0.024 mmol), TBAI (0.064 mmol) and CS_2 (8 mmol) was stirred at 70 or 90 ºC (for propylene oxide and styrene oxide, respectively) for 16 h. The reaction yield was determined by NMR.

3. Results and Discussion

The reaction of styrene oxide **1a** with CO_2 was used as a model reaction to gauge the activity of different Lewis acids (LA) under the following conditions: 0.6 mol% LA, 1.6 mol% TBAI as nucleophilic additive, 60 ºC, 4 atm, neat (Fig. 1). The highest yields were recorded using zinc(II) bromide and chloride. It is known that $NbCl_5$ can perform well in this reaction [75, 76]; however, its catalytic activity ($FeCl_3$ behaved similarly) was found to be inferior to that of the zinc salts under the above reaction conditions. The lower activity displayed by $MgCl_2$ (63%) is opposite to the previously shown result, where it was more active than zinc(II) chloride (90% vs. 65%) under the reported conditions [100 °C, 18 h, CO_2 (1 atm), DMF] [35] but could be explained in terms of its poor solubility in the epoxide and the better in DMF as a solvent. Some other Lewis acids tested proved to be less effective catalysts.

Due to the presence in the literature of several examples of the application of unsupported TBAX (tetrabutylammonium halide) [77, 78] and another ammonium, [79] phosphonium [80, 81] and imidazolium [82] salts in the title reaction, TBAI alone was tested in the carboxylation of styrene oxide **1a** but the yield of **2a** did not exceed 30% (Fig. 1).

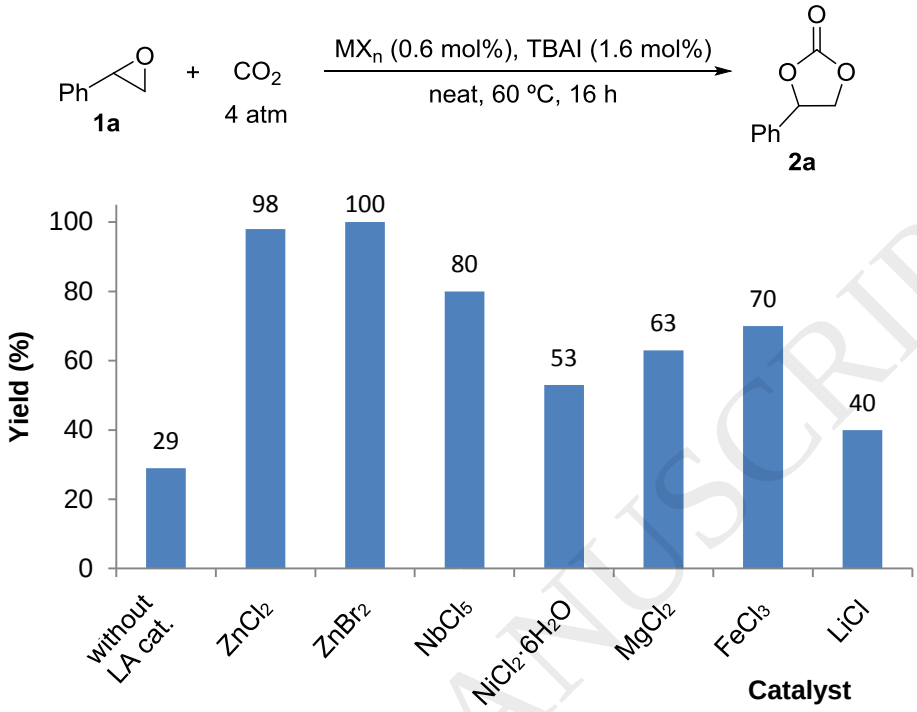


Fig. 1. Screening of Lewis acids (LA) in the synthesis of the cyclic carbonate **2a**.

Next, we explored a variety of inorganic supports for the most active metal salts in order to develop a recyclable catalyst, including silicon, aluminum, titanium and cerium oxides (Fig. 2). The best results were attained with the catalysts based on zinc salts on silica, alumina, titania and ceria as well as on boehmite and calcined Al_2O_3 (89–100%). In contrast, the oxide-supported niobium(V) and iron(III) chlorides showed very moderate activity (50% and 35% yield, respectively), not only lower than the activity of free LA but also comparable with that of the corresponding oxides. It is known that the silicon and aluminum oxides can catalyze themselves the reaction in the presence of a tetrabutylammonium salt [55], that is why their activity was also investigated. It turned out that the application of the SiO_2-TBAI system gave 60 and 45% yield of **2a** in 16 and 6 h, respectively, the Al_2O_3-TBAI system gave 45% in 16 h, but the conversion did not exceed 35% in the case of the titanium, zinc and cerium oxides. The results obtained show the phenomenon of a synergetic effect of addition of LA to the oxide, being positive in the case of zinc(II) salts (up to quantitative yield) and negative for $NbCl_5$ and $FeCl_3$ (10% decreased yields, from 60% to 50% and from 45% to 35% respectively). Among the most active catalysts, $ZnCl_2/SiO_2$, $ZnCl_2/Al_2O_3$ and $ZnCl_2/TiO_2$ allowed to get 100% yields in 6 h, which diminished to 50–74% for a shorter reaction time (2 h).

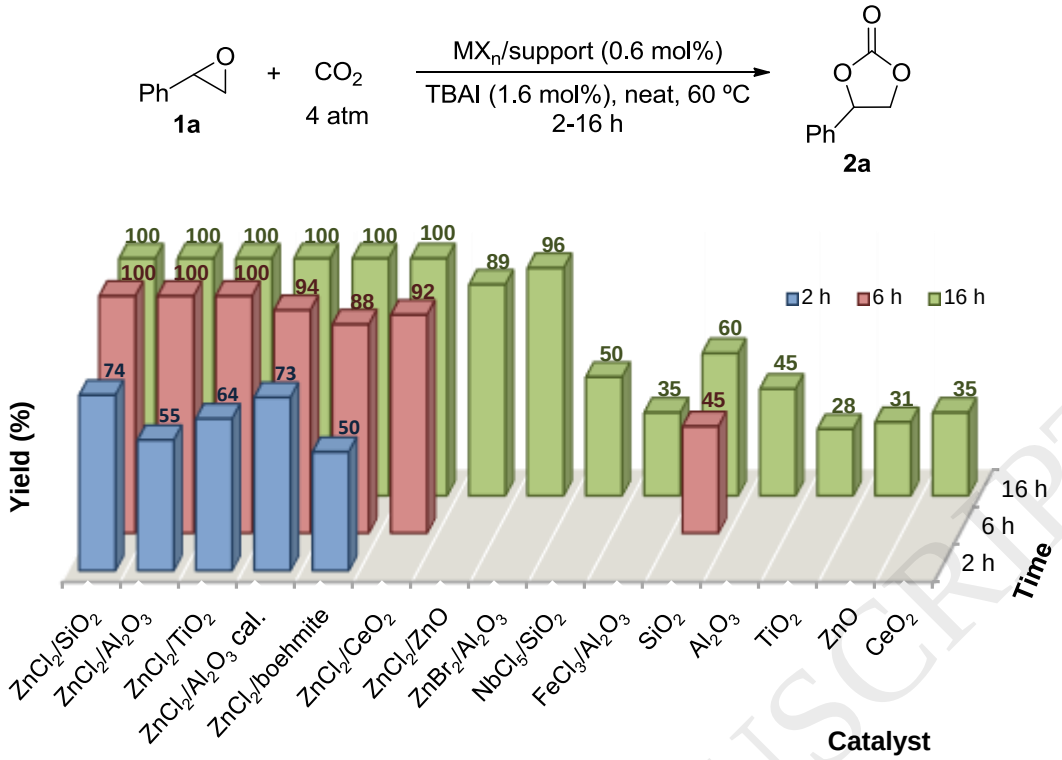


Fig. 2. Screening of supported catalysts and supports in the synthesis of the cyclic carbonate **2a**.

For further study, $ZnCl_2/Al_2O_3$ was considered the catalyst of choice due to its availability, air stability, low cost and easy application and isolation from the reaction mixture, especially, when compared with $ZnCl_2/TiO_2$; the lower impact of Al_2O_3 as catalyst on the reaction yield compared to that of SiO_2 was also taken into account. The kinetic data corresponding to the transformation of **1a** into **2a**, catalyzed by $ZnCl_2$ on three different alumina supports (Al_2O_3, calcined Al_2O_3 and boehmite), brought into view a higher initial reaction rate for $ZnCl_2/Al_2O_{3calcined}$ but with a trend to stabilization after 4 h (Fig. 3). Half-conversion was achieved in 2 h with both $ZnCl_2/Al_2O_3$ and $ZnCl_2$/boehmite but full conversion was accomplished faster with the former. Such effect could be caused by the difference in morphology of the surface of the supports as well as by the number of hydroxyl groups on it.

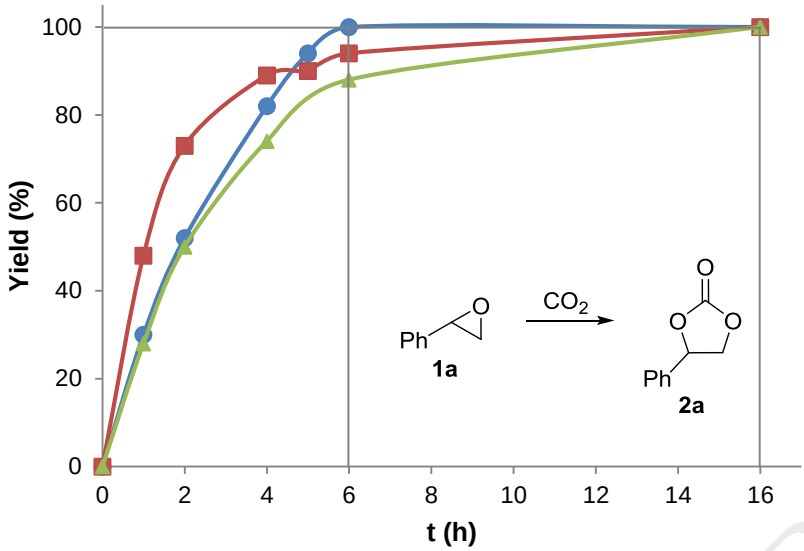


Fig. 3. Kinetic profiles for the synthesis of **2a** catalyzed by $ZnCl_2/Al_2O_3$ (●), $ZnCl_2/Al_2O_{3calcined}$ (■) and $ZnCl_2$/boehmite (▲). Reaction conditions: **1a** (4.0 mmol), catalyst (0.6 mol%), TBAI (1.6 mol%), neat, 60 ºC, 4 atm.

The structural morphology of the catalyst surface and its composition were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). SEM images (Fig. 4) before (a) and after (b) the carboxylation process do not show any noticeable changes in the catalyst surface morphology. EDX spectra of these two samples display a close to 2:3:23:33 Cl/Zn/Al/O molar ratio, which corresponds to the structure $Zn_3Cl_2Al_{22}O_{33}$ and supports the formation of Cl-Zn-O-Al bonds on the surface of alumina.

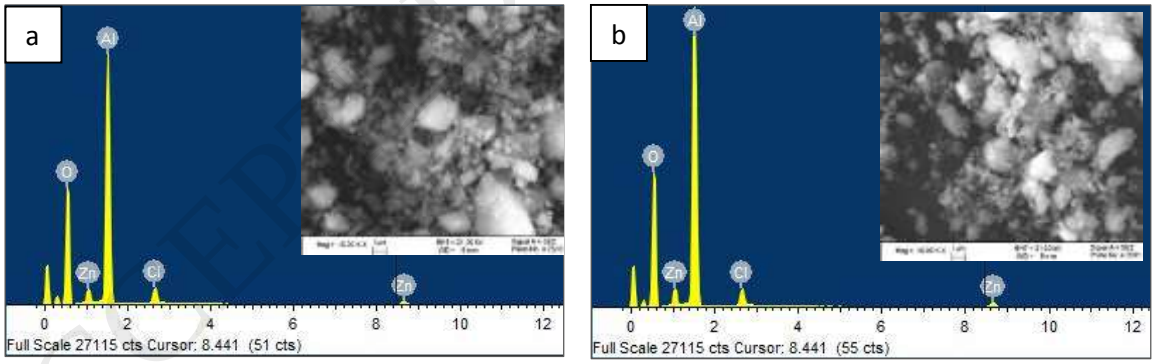


Fig. 4. SEM micrographs and EDX spectra of a $ZnCl_2/Al_2O_3$ sample before (a) and after (b) the reaction.

FT-IR/ATR investigation of the catalyst was performed for its precursors (pure $ZnCl_2$ and Al_2O_3) and a sample containing larger amount of LA (40 wt%), in order to increase the intensity of the Zn-element signals in the spectra. As shown in Fig. 5, the intensity of the peak at 1410 cm^{-1} (vw), corresponding to Zn-Cl bond of the catalyst, decreased in comparison with the corresponding slightly shifted peak at 1404 cm^{-1} (s) of the $ZnCl_2$ sample. The absorption bands at 1610 cm^{-1} and 3466 cm^{-1} correspond to deformation and stretching vibrations of the OH-water groups, respectively, less

intensive in the catalyst sample. The decrease of intensity of the Zn-Cl band and appearance of bands at 467, 580, 1069, 1155 and 3279 cm^{-1}, corresponding to Al-Cl, Zn-O and M-OH (M=Zn/Al) groups [83, 84] demonstrate the formation of a Cl-Zn-O-Al structure on the surface of the catalyst. The probable structure of the catalyst surface is given in the Fig.5. It is also supported by previous EXAFS (Extended X-Ray Absorption Fine Structure) analysis on the interaction between $ZnCl_2$ and the alumina matrix in a rhenium-catalyzed olefin metathesis revealed that Zn was coordinated to both, the surface O and Cl (where Zn/Cl = 1) [85].

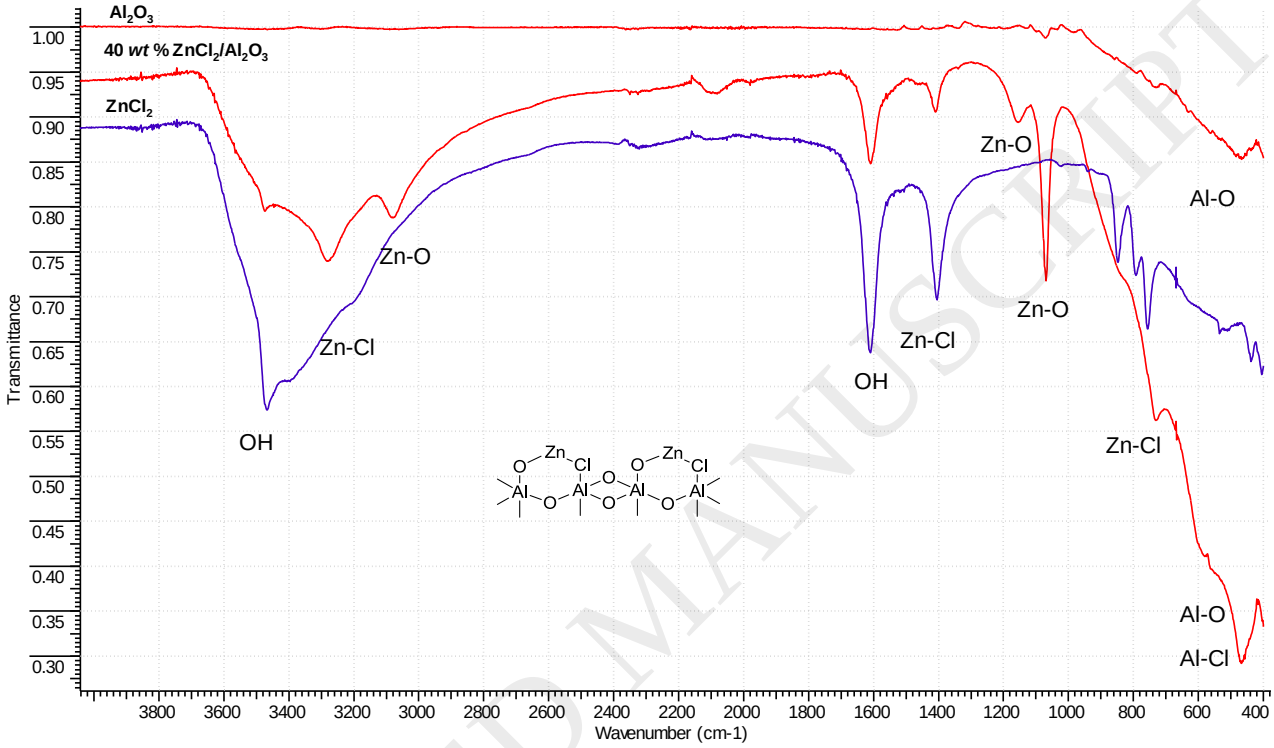


Fig. 5. FT-IR spectra of Al_2O_3, LA ($ZnCl_2$) and LA (40 wt %) on alumina support, and probable structure of the catalyst.

The powder XRD patterns (Fig. 6) of $ZnCl_2/Al_2O_3$ (10 wt%) and Al_2O_3 samples exhibit characteristic peaks of the aluminum oxide support (2θ values of 17.1º, 33.1º, 45.2º, 54.2º, 57.8º, 58.3º, 65.8º and 72.1º). Characteristic peaks of crystalline $ZnCl_2$ were not observed in the 10 wt% catalyst. The same effect was previously found for silzic ($ZnCl_2/SiO_2$) catalyst obtained by a similar technique [86]. The PXRD pattern of a $ZnCl_2/Al_2O_3$ (40 wt%) exhibits characteristic peaks of the zinc chloride (2θ values of 28.9º, 30.0º, 31.0º, 32.6º, 34.5º, 41.1º and 50.9º) and ZnO (2θ values of 32.0º, 34.5º, 36.8º, 49.1º and 57.5º) as well as peak of aluminum hydroxide (2θ value of 18.7º) corresponding to those published before [87, 88]. The presence of a large bump distributed in a wide range 10–28º 2θ indicates the presence of an amorphous phase in the catalyst samples, the intensity of which is proportional to the amount of $ZnCl_2$.

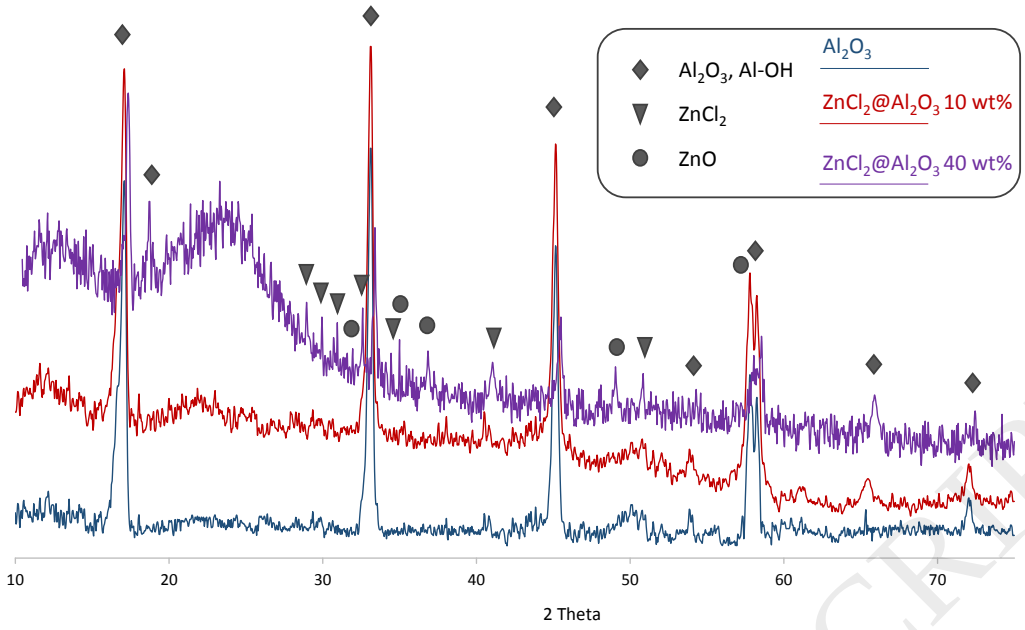


Fig. 6. X-ray diffraction spectrum of the powder samples of Al_2O_3 (blue), $ZnCl_2$(10 wt%)/Al_2O_3 (red) and $ZnCl_2$(40 wt%)/Al_2O_3 (purple).

The porous structure of the catalyst and alumina support was determined by BET analysis. As shown in Fig. 7, after $ZnCl_2$ loading, N_2 adsorption and desorption isotherms have a typical trend, the support's BET surface area slightly decreased from 130 to 116 m^2/g, and the pore volume determined at p/p^o = 0.99 was reduced from 0.221 to 0.197 mL/g.

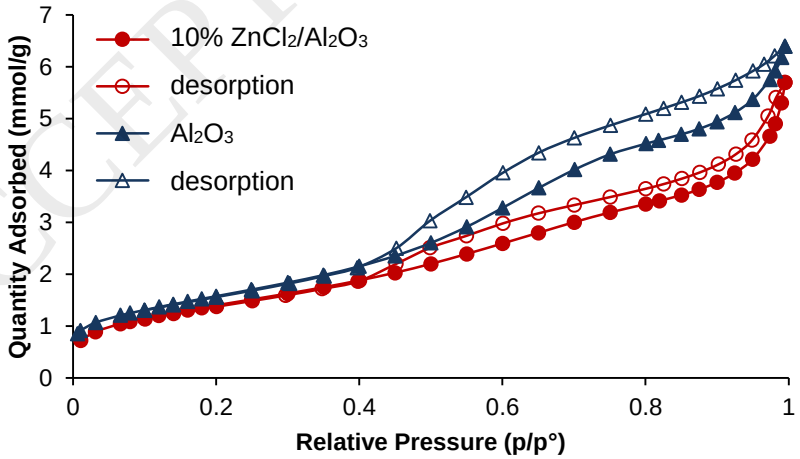


Fig. 7. N_2 adsorption/desorption isotherms of Al_2O_3 (▲/▲) and 10 wt% $ZnCl_2$/Al_2O_3 (●/●)

The pore-size distribution curves determined by the BJH method (Fig. 8) for alumina and both samples of the freshly prepared and recovered catalyst show one narrow mode, corresponding to average pore sizes of 6.68 nm for alumina, and 6.45 nm and 6.56 nm for $ZnCl_2/Al_2O_3$ before and after the reaction, respectively. No pores smaller than 2 nm were observed. The absence of micropores could have a positive effect on the catalytic process, since the rate of the reaction is determined only by the rate of adsorption of reagents by the active catalytic centers, the formation of products and its desorption. The absence of significant changes in the pore distribution (<5%) of the catalyst after the reaction suggests a very promising recycling behavior.

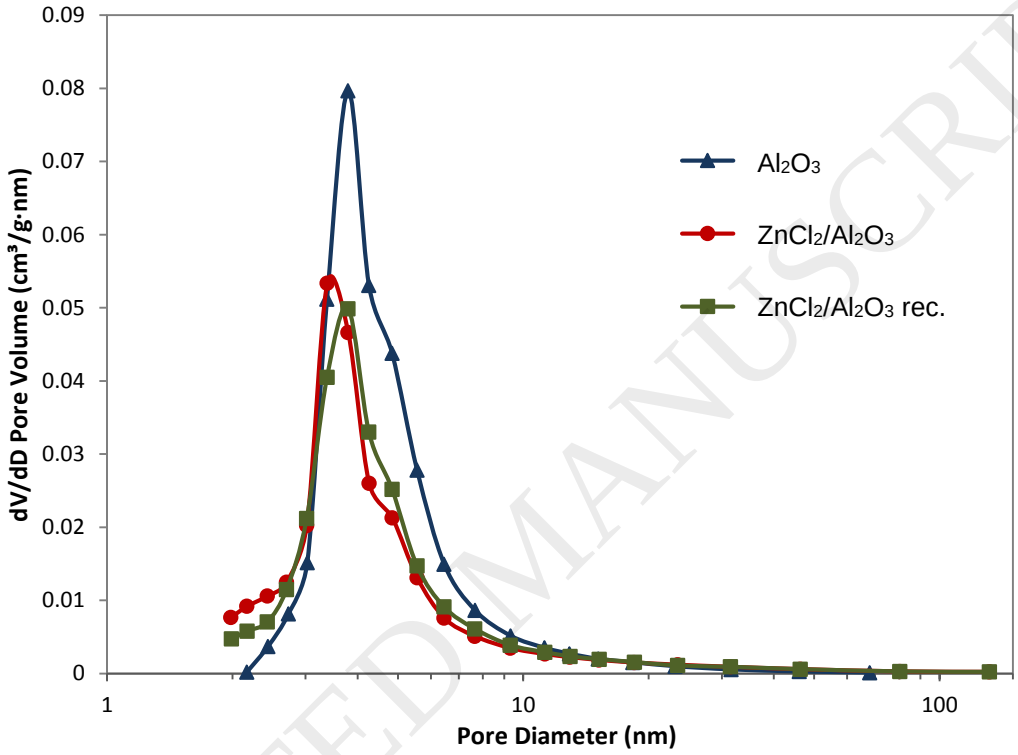
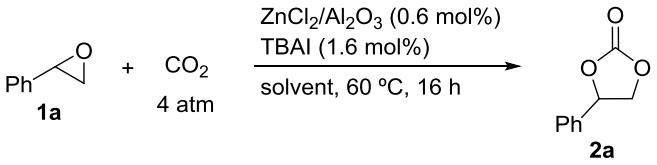


Fig. 8. Pore-size distribution of Al_2O_3 (▲) and $ZnCl_2/Al_2O_3$ samples before (●) and after (■) styrene oxide (**1a**) carboxylation.

Generally, the synthesis of cyclic carbonates from epoxides proceeds under Lewis acid catalysis in solvent-free media, owing to the fact that the epoxide can serve itself as a solvent at the initial stage and, afterwards, the carbonate generated during the reaction can play this role. The positive effect of carbonates as solvents on the reaction rate was previously described in the literature [89]. We observed that solvents such as methyl ethyl ketone or dioxane gave very modest yields of **2a** under the above conditions (Table 1, entries 2 and 3), though the deleterious effect on the yield was more dramatic for toluene (Table 1, entry 1). On the contrary, ethylene carbonate as a solvent afforded quantitative yield of **2a** in 16 h (Table 1, entry 5). Gratifyingly, the best result was obtained under solvent-free conditions, with a full conversion being reached in 6 h (Table 1, entry 6).

Table 1. Screening of solvents in the synthesis of **2a**.[a]

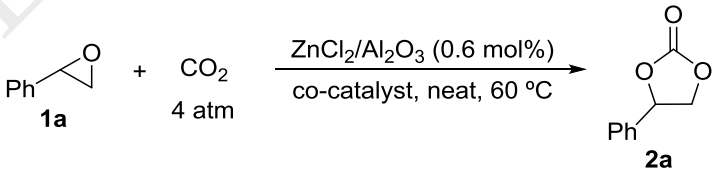


Entry	Solvent	Yield (%)[a]
1	Toluene	<5
2	Dioxane	33
3	Methyl ethyl ketone	44
4	Ethylene carbonate	100
5	Neat	100
6	Neat	100[b]

[a] Yield determined by NMR based on **1a**.[b] 6 h.

Then, the activity of ammonium salts as nucleophilic additives was examined. In a control experiment, the necessity for this type of agent was proven to be indispensable (Table 2, entry 1). As it has been mentioned above (Fig. 1), TBAI promotes the reaction by itself but in very poor yield (Table 2, entry 2). But in combination with Lewis acid TBAI or TBAB led to nearly quantitative yield when applied at 1.6 mol% loading for 16 h (Table 2, entries 3 and 4). However, TBAI was found to be superior to TBAB when reducing either the loading or the reaction time (Table 2, entries 5–8), what could be explained by the larger polarizability and leaving group ability of iodide compared to those of bromide. It is noteworthy that the addition of small amounts of TBAI to TBAB (TBAI/TBAB = 0.1–0.3) accelerated the reaction affording 92% yield in 6 h (Table 2, entries 9 and 10). The TBAI/TBAB mixture effect was also evinced in the reaction catalyzed by unsupported zinc(II) chloride (Table 2, entry 11). Therefore, TBAI (1.6 mol%) was chosen as the optimum nucleophilic additive for further investigations. But for the scaling and cheapening of the process the combination of TBAB and TBAI looks more promising.

Table 2. Screening of nucleophilic additives in the synthesis of **2a**.

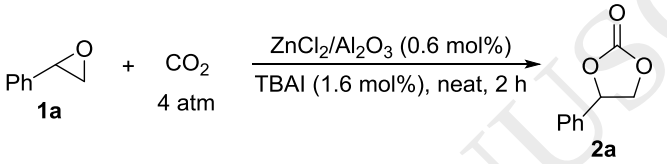


Entry	Additive (mol%)	Time (h)	Yield (%)[a]
1	-	16	<1
2	TBAI (1.6)	16	29[b]
3	TBAI (1.6)	16	100
4	TBAB (1.6)	16	97
5	TBAI (0.2)	6	38
6	TBAI (0.6)	6	74
7	**TBAI (1.6)**	**6**	**100**

8	TBAB (1.6)	6	70
9	TBAB (1.2) + TBAI (0.4)	6	92
10	TBAB (1.44) + TBAI (0.16)	6	91
11	TBAB (1.44) + TBAI (0.16)	6	92[c]

[a] Yield determined by NMR based on **1a**. [b] Without Lewis acid catalyst.
[c] Unsupported $ZnCl_2$ as catalyst.

The influence of the temperature and CO_2 pressure on the carboxylation of **1a** was also assessed for a reaction time of 2 h (Fig. 9). The yield upgrade experienced when increasing either the temperature or the pressure was previously pointed up in the synthesis of cyclic carbonates [74]. The same trend was recorded in our case: the product yield rose from 39% at 40 ºC to 55% at 60 ºC, and to 79% at 80 ºC; every 2 atm increment of the CO_2 pressure increased the yield in 6–15%. The reaction carried out under the mildest conditions (rt, 1 atm. CO_2) was significantly slowed down and gave 82% yield in 24 h.



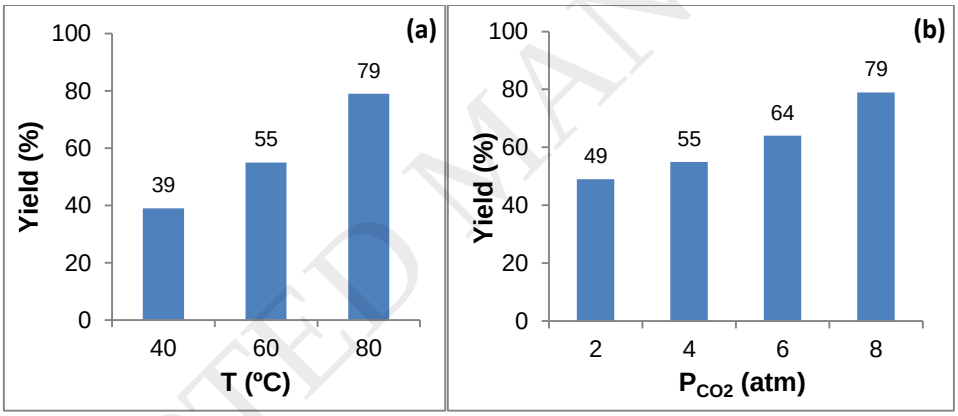


Fig. 9. Study of the effect of (a) the temperature (P_{CO2} = 4 atm) and (b) the CO_2 pressure (T = 60 ºC) on the yield of the carboxylation of epoxide **1a**.

The optimal conditions (60 ºC, 4 atm, CO_2), efficient and quite mild and economic, were applied to the aromatic and aliphatic epoxides styrene (**1a**) and propylene (**1b**) oxides, respectively, in order to compare their kinetic profiles (Fig. 10). Both cyclic carbonates (**2a** and **2b**) were formed in quantitative yield but the rate of formation of **2b** was considerably higher than that of **2a**. This behavior could be explained, in part, by steric effects, as previously observed in the reaction of epoxides bearing bulky substituents catalyzed by sterically hindered aluminum complexes [90] or heterogeneous catalysts [91]. However, electronic effects can play a more dominant role because of the better delocalization of the negative charge on the styrene-derived alkoxide intermediate, which reduces its nucleophilic character and, subsequently, attenuates the reaction of the alkoxide with CO_2 and, in turn, the reaction rate [92].

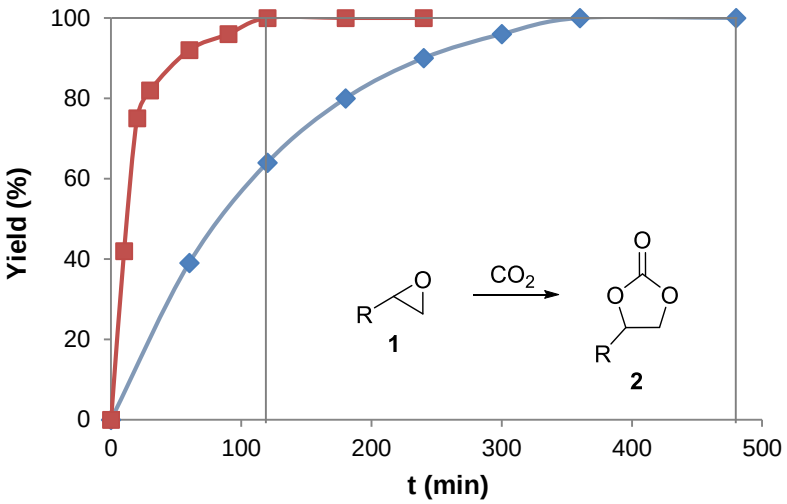


Fig. 10. Kinetic profiles for the carboxylation of styrene (**1a**, ♦) and propylene (**1b**, ■) catalyzed by $ZnCl_2/Al_2O_3$-TBAI. Reaction conditions: **1a** (4.0 mmol), catalyst (0.6 mol%), TBAI (1.6 mol%), neat, 60 ºC, 4 atm.

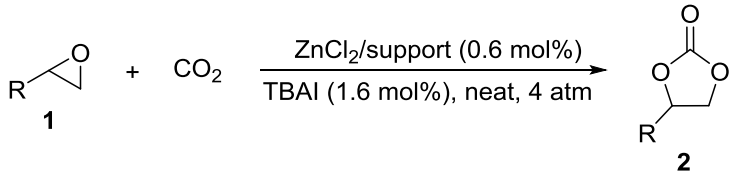
We extended the optimized conditions to a range of differently substituted oxiranes (Table 3). Both styrene oxide (**1a**) and propylene oxide (**1b**) were quantitatively transformed into the corresponding cyclic carbonates **2a** and **2b** irrespective of using alumina or titania as supports; as pointed out above, **1b** reacted faster than **1a** even at a pressure of 2 atm. An increase in the length of the alkyl chain, as in 2-hexyloxirane (**1c**), made the reaction slower when compared with propylene oxide (**1b**). The reaction conditions were compatible with the presence of a carbon-carbon double bond (**1d**) or chlorine atom (**1e**) in the starting epoxide; a possible chloro-iodo exchange in **2e** was not detected. The yield of the chloroaromatic carbonate **2f** was substantially improved just by increasing the reaction time from 6 to 8 h. Quantitative yields were also noted for epoxides **2g** and **2h**, albeit higher temperature or longer reaction time were necessary, with the presence of ethylene carbonate preventing solidification of the reaction mixture because of the high-melting of the products **2g** and **2h**.

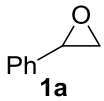
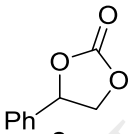
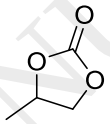
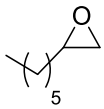
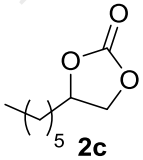
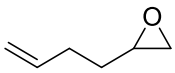
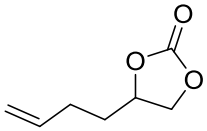
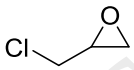
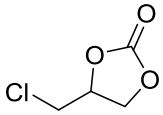
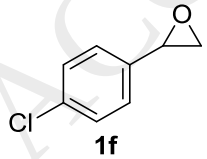
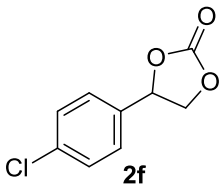
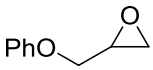
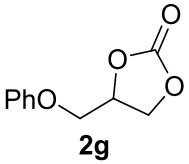
It is known that disubstituted epoxides are more reluctant to react with CO_2 than the monosubstituted counterparts, especially when they have a bicyclic structure [35, 44, 46]. For instance, 1,1-dimethyloxirane (**1i**) gave the expected carbonate **2i** in moderate yield after 16 h. The carboxylation of the cyclic epoxides **1j** and **1k** was better effected with the more active $ZnBr_2/Al_2O_3$ catalyst under harsher conditions (8 atm, 80 ºC) and double catalyst loading (1.2 mol% for **1k**). At any rate, their conversion was incomplete leading to the *cis* bicyclic carbonates **2j** and **2k** in 76% and 39% yield, respectively.

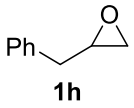
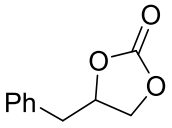
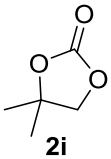
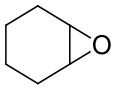
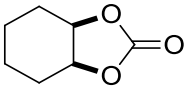
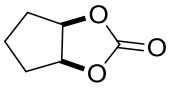
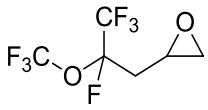
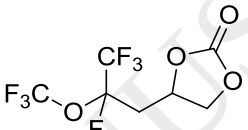
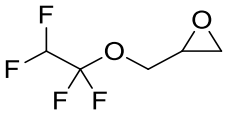
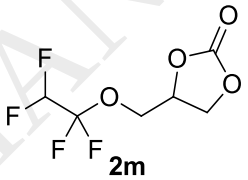
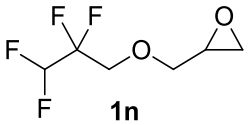
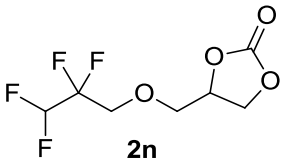
Fluorinated carbonates are used as electrolytic additives in Li-ion [93, 94] and Na-ion [95] batteries for increasing capacity, oxidation resistance and incombustibility. The simplest route to this type of

compounds is the direct fluorination [96], though it results in a mixture of products because of the lack of selectivity. Our proposed carboxylation of the fluorinated epoxides **1l-n** provided the desired carbonates under moderate temperature and pressure (70 ºC, 6 atm). Moreover, the use of the less active TBAB instead of TBAI was also efficient. It is worthy of note that the cyclic carbonates **2l-m** are new polyfluorinated products and were obtained in quantitative yields with 100% selectivity.

Table 3. Reaction of epoxides **1** with CO_2.[a]



Epoxide	Catalyst	T (ºC)	t (h)	Product	Yield (%)[b]	TON/TOF[c]
 **1a**	$ZnCl_2/Al_2O_3$	60	6	 **2a**	100	167/28
	$ZnCl_2/TiO_2$	60	6		100	–[nd]
 **1b**	$ZnCl_2/Al_2O_3$	60	2	 **2b**	100	167/83 833[d]/417[d]
	$ZnCl_2/TiO_2$	60	2		100	–[nd]
	$ZnCl_2/Al_2O_3$	60	2		97[e]	–[nd]
 **1c**	$ZnCl_2/Al_2O_3$	60	16	 **2c**	100	167/10
		60	6		98	163/27
 **1d**	$ZnCl_2/Al_2O_3$	60	6	 **2d**	100	167/28
 **1e**	$ZnCl_2/Al_2O_3$	60	6	 **2e**	87	145/24
 **1f**	$ZnCl_2/Al_2O_3$	60	6	 **2f**	80	133/22
		60	8		96	160/20
 **1g**	$ZnCl_2/Al_2O_3$	60	3	 **2g**	70	–[nd]
		100	4		100	167/42
		60	16		100[f]	–[nd]

 **1h**	$ZnCl_2/Al_2O_3$	100	4	 **2h**	100[f]	167/42
 **1i**	$ZnCl_2/Al_2O_3$	60	16	 **2i**	61	102/6
 **1j**	$ZnCl_2/Al_2O_3$	60	16	 **2j**	11[g]	–[nd]
		100	16		34[g]	57/4
		110	32		60[h]	100/3
	$ZnBr_2/Al_2O_3$	60	16		21[g]	–[nd]
		80	24		76[i]	127/5
 **1k**	$ZnBr_2/Al_2O_3$	80	16	 **2k**	39[i]	33/2
 **1l**	$ZnCl_2/Al_2O_3$	70	24	 **2l**	100[h,j]	167/7
 **1m**	$ZnCl_2/Al_2O_3$	70	24	 **2m**	100[h,j]	167/7
 **1n**	$ZnCl_2/Al_2O_3$	70	24	 **2n**	100[h,j]	167/7

[a] Reaction conditions: **1** (4.0 mmol), catalyst (0.6 mol%), TBAI (1.6 mol%), neat, 4 atm. [b] Isolated yield. [c] TON (turnover number: $mmol_{product}/mmol_{catalyst}$) and TOF (turnover frequency: $mmol_{product}/(mmol_{catalyst} \cdot time)$, h^{-1}) were determined under optimal conditions for each substrate. [d] TON or TOF in 5 cycles. [e] 2 atm. [f] In ethylene carbonate. [g] Yield determined by NMR. [h] 6 atm. [i] 8 atm. [j] TBAB.

The recyclability of the catalyst was examined in the carboxylation of propylene oxide (**1b**) as the most reactive substrate (Fig. 11). The catalytic system $ZnCl_2/Al_2O_3$-TBAI could be reused, at least, five times without loss of activity. Recycling tests with incomplete conversion (75% in 20 min) of **1a** were successfully carried out and no drop in activity upon catalyst recycling was observed. Interestingly, not only $ZnCl_2/Al_2O_3$ could be recovered by centrifugation from the reaction crude, but up to 80% of the amount of TBAI was also recycled by precipitation from the centrifuged mixture with diethyl ether, and added to a new loading of reagents.

When compared with other catalytic systems, $ZnCl_2/Al_2O_3$-TBAI is readily available, active under quite mild conditions [compare with 55, 57–60, 64–70] and recyclable. Moreover, it works in the

absence of ligands [23, 39, 40, 47, 48] with an activity not inferior to that of other heterogeneous catalysts [55, 57–66, 68–70].

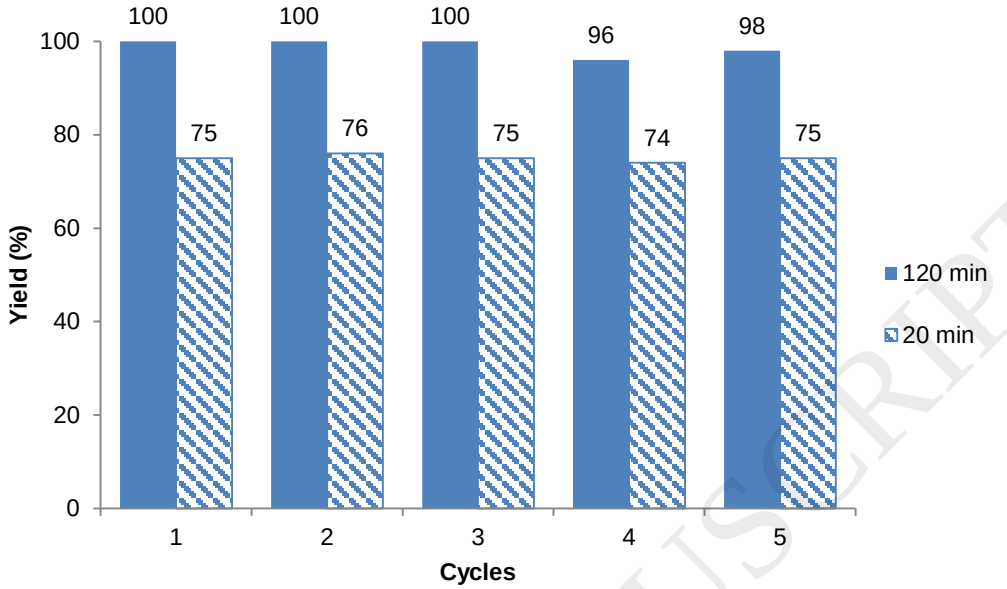
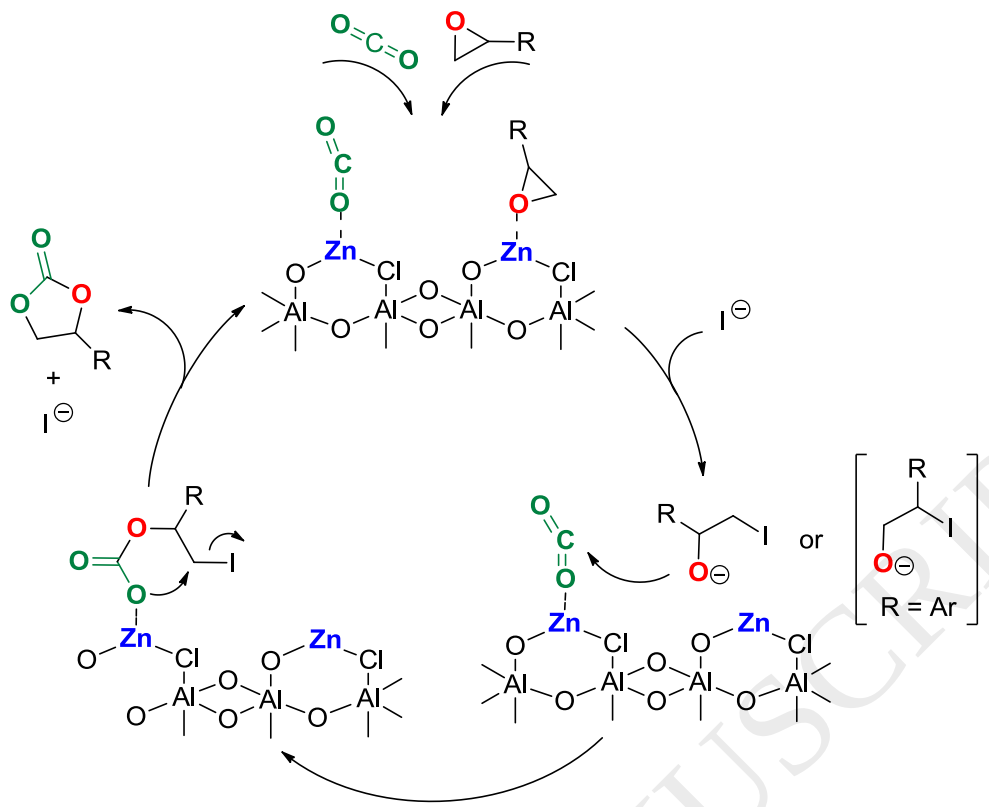


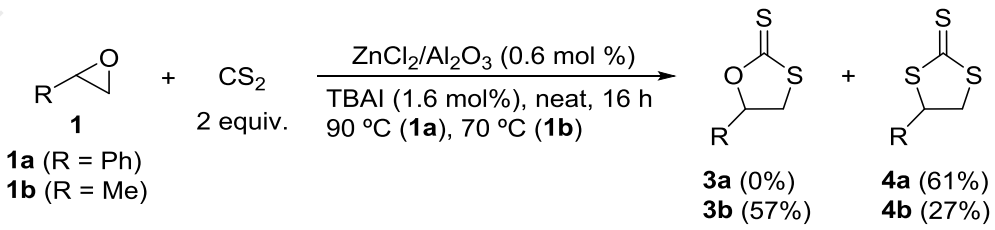
Fig. 11 Recycling of $ZnCl_2/Al_2O_3$ in the synthesis of propylene carbonate **2b**. Reaction conditions: **1b** (4.0 mmol), $ZnCl_2/Al_2O_3$ (0.6 mol%), TBAI (1.6 mol%), 60 ºC, 4 atm, 2 h (■) or 20 min (⊟).

A reaction mechanism for the catalytic carboxylation of epoxides on the $ZnCl_2/Al_2O_3$ surface was put forward (Scheme 1). First, it seems reasonable to suggest that Zn could activate both CO_2 [92, 97, 98] and the epoxide [92] by intensifying their electrophilicity. The coordination of Zn on the surface of Al_2O_3 to the epoxide is also supported by the appearance in the FT-IR spectrum of the broad intense bands (at 1132 cm^{-1} and 1157 cm^{-1}), probably attributed to the stretching modes of Zn–O–C group along with the characteristic C–O–C band of epoxide ring at 1259 cm^{-1} (See ESI for spectra). Iodide ion attack on the terminal or internal oxirane carbon of the alkyl or aryl-substituted epoxides [99–101], respectively, would furnish the alkoxide species ready to add to CO_2. Intramolecular 5-*exo*-*tet* cyclization of the acyclic mixed carbonate would release the cyclic carbonate and iodide ion, with the latter entering the catalytic cycle again.



Scheme 1. Reaction mechanism proposed for epoxide carboxylation catalyzed by $ZnCl_2/Al_2O_3$-TBAI.

Carbon disulfide is an easily available and inexpensive building block for organic synthesis, widely used in the chemical industry. Although CS_2 is an isoelectronic heterocumulene of carbon dioxide, its reaction with epoxides has been much less explored. The reaction results, in most cases, in a mixture of the 1,3-oxathiolane-2-thione and 1,3-dithiolan-2-thione as well as in 1,3-dithiolane-2-ones, 1,3-oxathiolane-2-ones, 1,3-dioxolane-2-thiones and thiiranes [102–104]; therefore, good functional group selectivity is the most important goal to achieve in this process. The same catalytic system optimized for the carboxylation of epoxides was tested in the thiocarboxylation variant with a minimum amount of CS_2. Propylene oxide (**1b**) reacted with full conversion at 70 ºC for 16 h producing a mixture of the propylene di- and trithiocarbonates **3b** and **4b** (57% and 27% yield, respectively). In contrast, the reaction of styrene oxide (**1a**) with CS_2 was far more selective, giving rise to styrene trithiocarbonate **4a** in 61% yield at 90 ºC (Scheme 2).



Scheme 2. Reaction of epoxides **1a** and **1b** with CS_2 catalyzed by $ZnCl_2/Al_2O_3$-TBAI.

Conclusions

The results of this study suggest a new avenue for research on epoxide carboxylation based on heterogeneous catalysis: the first heterogeneous $ZnCl_2$-catalyzed carboxylation of epoxides in the presence of a tetrabutylammonium halide has been presented. A thorough comparison of the activity of different Lewis acids and their supports led to the conclusion that $ZnCl_2/Al_2O_3$ was the catalyst of choice for the title reaction because of being efficient, cheap and easily prepared and applied. When combined with tetrabutylammonium iodide as nucleophilic additive, the obtained catalytic system has allowed to perform the reaction under relatively mild (typically, 60 ºC, 4 atm) and solvent-free conditions. Most of the monosubstituted carbonates have been synthesized in quantitative yields, including novel polyfluorinated ones, whereas disubstituted epoxides were more averse to react. The activity at low catalyst loading (0.6 mol% $ZnCl_2$, 1.6 mol% TBAI) is comparable or superior (in some cases) to that of other more complex heterogeneous catalysts or homogeneous aluminum complexes. Both, the catalyst ($ZnCl_2/Al_2O_3$) and the quaternary ammonium salt (TBAI) have been easily recovered and successfully reused in five cycles with no loss of activity. This fact, together with the small amounts of zinc and ammonium salts deployed, the solvent-free medium and the moderate temperature and pressure employed, makes the process economically and ecologically attractive and sustainable. Furthermore, the aforementioned catalytic system has been shown to be also effective in the reaction of epoxides with carbon disulfide to form di- or trithiocarbonates.

Acknowledgments

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